but in the formation of 16, the carbone carbon moves toward the o-methyl group. Products 13 and 19 show that the first few steps of the mechanism in Scheme I are reversible and that carbene 14 can close to 13 or undergo a hydrogen transfer to give the o-quinodimethane 20 and that some of 13 or 20 can rearrange to 19.

Thus the results of our labeling experiments are consistent with the conclusion that the major pathway for the rearrangement of 1 to 2 involves a series of arylcarbene-cycloheptatetraene interconversions

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Use of η^6 -Arylphosphine Complexes of Molybdenum(0) for the Synthesis of Complexes Containing Mo⁴Mo and Mo-W Bonds

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The three heterobimetallic complexes known to have quadruple metal-metal bonds are $CrMo(O_2CMe)_4$,¹ MoW(O₂CCMe₃)₄,² and $MoW(mhp)_4$.³ In each case the quadruple bonds are bridged by bidentate ligands: acetate, pivolate, or 2-hydroxy-6-methylpyridine anion, respectively. Complexes containing the homo-

nuclear quadruple bonds $Mo^{4}_{-}Mo$ or $W^{4}_{-}W$ with and without bridging ligands have been well studied,⁴ including complexes $Mo_2Cl_4(PR_3)_4^{5-9}$ and $W_2Cl_4(PR_3)_4^{5,10,11}$ where PR₃ is a tertiary phosphine ligand. We report here the very efficient synthesis of $MoWCl_4(PMePh_2)_4$, which contains the first heterobimetallic quadruple bond that is not supported by bridging ligands. The properties of this bond can be compared for the first time with

Mo⁴-Mo and W⁴-W bonds that are free of bridging ligands. Our synthesis of MoWCl4(PMePh2)4 involves two novel features: first, the reaction of a mononuclear complex of Mo(0) with chloride

compounds of Mo(IV) or W(IV) to give $Mo^{4}M$ dimers (eq 1);

$$Mo(0) + M(IV) \rightarrow Mo^{-4}M \qquad M = Mo, W \qquad (1)$$

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Scheme I



 $L = PMePh_2, L^* = PMe_3$

Table I. ³¹P NMR Data for 5 (in C_6H_6 vs. 85% H_3PO_4) and $W_2Cl_4P_4$ (6),¹⁰ P = PMePh₂

isotopomer	$\delta(^{31}\mathbf{P}), \text{ ppm}$	J _{PP} ³ , Hz	$J_{\rm PW}^2$, Hz	$J_{\rm PW}^{1}$, Hz	
W-Mo-P	-13.1 t	23.5			
¹⁸³ W ⁴ Mo-P	-13.1 dt	23.5	43		
P-W ⁴ Mo	21.9 t	23.5			
P-183W-Mo	21.9 dt	23.5		266	
$^{183}W_{-}^{4}W(6)$	2.0 m	28	51	234	_

second, the use of a Mo(0) complex containing an η^6 -PhPMePh

ligand to give a Mo^4M compound in a regiospecific reaction. During our study of the use of derivatives of $Mo(\eta^6$ -PhPMePh)(PMePh₂)₃ (1) as phosphine-like ligands,¹² we discovered that complex 1 reacted with $MoCl_4(THF)_2^{13}$ (2) after stirring for 10 h in degassed tetrahydrofuran (THF) at 22 °C to give the known complex $Mo_2Cl_4(PMePh_2)_4^{7,14}$ (3) in its green form¹⁴ (Scheme I). Precipitation with hexanes and recrystallization from benzene/hexanes gave 3 as its blue isomer¹⁴ in 75% yield. The dinitrogen complex trans- $Mo(N_2)_2(PMePh_2)_4$ also reacted with 2 to give 3. Complex 3 was identified by C, H analysis and ³¹P NMR.¹⁴ The blue isomer in benzene had a visible absorption ($\delta \rightarrow \delta^*$) at 596 nm and a Raman active mode, ν -

(Mo-Mo), at 349 cm⁻¹ in agreement with literature values.¹⁴

The new complex $MoWCl_4(PMePh_2)_4$ (5)¹⁵ is prepared according to Scheme I by adding a benzene solution of 1 dropwise to a 3-fold excess of WCl₄(PPh₃)₂ (4)¹⁶ suspended in dry benzene under N₂. The reaction is instantaneous at 22 °C; excess 4 is filtered off after 5 min and green complex 5, contaminated with approximately 5% 3, is crystallized with hexanes. Complex 3 is the only detectable side product; however, if traces of water are present then side reactions give WOCl₂(PMePh₂)₃¹⁷ as well as complex 3. Complex 3 cannot be separated from 5 by chromatography, but 3 can be fairly selectively converted by reaction with

(15) Anal. Calcd for $C_{52}H_{52}MoWP_4Cl_4 \cdot 0.2C_6H_6$: C, 51.60; H, 4.33. Found: C, 51.62; H, 4.51. (16) Butcher, A. V.; Chatt, J.; Leigh, G. J.; Richards, R. L. J. Chem. Soc.,

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PMe₃ at 20 °C to soluble derivatives which then remain in solution when pure 5 (60% yield) is precipitated with hexanes.

Significantly if $Mo(N_2)_2(PMePh_2)_4$ is used in place of 1 in the reaction then a mixture of 3 (35% based on the starting Mo complex 1), 5(20%), and $WOCl_2(PMePh_2)_3$ (30%) is formed. Thus the regiospecificity of the reaction could be attributed to the ability of 1 to coordinate via the η^6 -ligand to the tungsten and hence favor heterobimetallic bonding. $^{12}\,$ The complex $W_2Cl_4\text{-}$ $(PMePh_2)_4$ (6)¹⁰ is not produced in any of these reactions. Preliminary work shows that MoWCl₄(PMe₂Ph)₄¹⁸ is produced when $Mo(\eta^{6}-PhPMe_{2})(PMe_{2}Ph)_{3}^{19}$ is used in place of 1 in Scheme I. Complex 5 is most readily identified by the coupling constants

of the inequivalent phosphorus atoms on the ${}^{183}W_{-}^{4}Mo$ isotopomer in the ³¹P NMR spectrum. The J values are similar to those

observed for the $^{183}W-W$ isotopomer of complex 6 (Table I). The ¹H NMR spectrum of 5 in C₆D₆ shows two methyl resonances as virtual triplets at 1.90 and 2.07 ppm and two sets of ortho phenyl proton multiplets at 7.56 and 7.73 ppm consistent with two types of phosphines, whereas 3 gives only one methyl peak at 1.98 ppm and one ortho proton multiplet at 7.65 ppm. The λ_{max} (visible) of 5 in benzene at 650 nm falls in the range of $\delta \rightarrow \delta^*$ transitions of homonuclear complexes, ^{5,8,14,20} including Mo₂Cl₄(PMe₃)₄ at 582 nm^5 and $W_2Cl_4(PMe_3)_4$ at 657 nm.⁵ It is interesting that the

 Mo_{--}^{4} W complex with bridging carboxylates² has a yellow color; perhaps a $\delta \rightarrow \pi^*$ (ligand) transition, recently observed in the 500-600 nm region for $W_2(O_2CR)_4$ complexes,²¹ complicates the visible spectrum when these bridging ligands are present. No

frequency (IR or Raman) assignable to $\nu(Mo^4W)$ is observed in the range 250-400 cm.⁻¹ Solutions of 5 are sensitive to water and oxygen. Complex 5 decomposes when refluxed in degassed toluene; it does not disproportionate to 3 and 6.

The substitution reactions of 5 are proving to be fascinating. For example, 5 reacts with excess PMe₃ at 20 °C for 3 h to give

 $(Me_3P)_2Cl_2Mo - WCl_2(PMePh_2)_2$ (7)²² where only the phosphines on the molybdenum have been substituted. Further reaction (45 °C, 19 h) gives MoWCl₄(PMe₃)₄.²³ The course of reaction differs from that reported for $Mo_2Me_4(PEt_3)_4$.²⁴

The structure of 5 (Scheme I) is proposed on the basis of the D_{2d} geometry of the homonuclear complexes.⁵ Work is under way to obtain crystals of 5 or its derivatives suitable for X-ray dif-'raction in order to verify the structure and obtain further data on this unique heteronuclear bond.

Note Added in Proof. Preliminary X-ray crystallographic analysis of complex 7 confirms the geometry shown in Scheme I. The structure has refined to R = 3.8% in the space group I_2/a . The molybdenum-tungsten distance is 2.209 (1) Å. (Personal communication from Jeffrey F. Sawyer.)

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Supplementary Material Available: Preparation of 3 and 5 and ¹H and ³¹P NMR spectra of 5 (4 pages). Ordering information is given on any current masthead page.

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Synthesis of Anatoxin-a: Very Fast Death Factor

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A class of microalgae, the cyanophytes, contains several toxic strains, including Anabaena flos-aquae.¹ Graphic descriptions of the death of animals induced by such blue-green algae have been recorded.^{2,3} An alkaloidal toxin identified from these sources was shown⁴ to be 2-acetyl-9-azabicyclo[4.2.1]non-2-ene (anatoxin-a, 1), also designated "Very Fast Death Factor" (VFDF).³



This structural assignment was confirmed by X-ray concellography.⁵ Anatoxin-a has been shown to be a potent music sinic¹ and nicotinic agonist⁶ and has engendered synthetic interest.⁷⁻⁹

We report herein an efficient, nitrone-based entry to this interesting natural product. It was anticipated^{10,11} that the addition of 1-pyrroline 1-oxide (2) to trans-3,5-hexadien-2-ol (3)¹²⁻¹⁴ would exhibit the desired site selectivity and regioselectivity (cf., Scheme I) to afford the isoxazolidine $4a^{15}$ The latter, formed in 70% yield, upon oxidation with manganese dioxide (Celite, methylene chloride), produces the ketone 6a, which exhibits a clean quartet at δ 4.71 (J = 6.71 Hz), assignable to the C-5 proton (isoxaze)idine numbering).

Oxidative cleavage^{16,17} of the isoxazolidine ring with mchloroperbenzoic acid gives the nitrone 5 as the sole identifiable product in 79% yield. The product is a single regioisomer exhibiting a broad singlet in its ¹H NMR spectrum (CDCl₁) 7.0 ppm (1 H) characteristic of the proton at C-2 of the nitrone function. Warming of a solution containing the nitrone to 45 °C leads to the formation of a single cycloadduct, 6a in 71% overall

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